Major Effects in the Thermodynamics of Detonation Products: Phase Segregation versus Ionic Dissociation

S. Bastea, L. E. Fried

March 11, 2010

Disclaimer

This document was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor Lawrence Livermore National Security, LLC, nor any of their employees makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or Lawrence Livermore National Security, LLC. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or Lawrence Livermore National Security, LLC, and shall not be used for advertising or product endorsement purposes.

Major Effects in the Thermodynamics of Detonation Products: Phase Segregation versus Ionic Dissociation

Sorin Bastea and Laurence E. Fried

Lawrence Livermore National Laboratory
7000 East Avenue, Livermore, CA 94550, USA

Abstract. Water (H_2O) and nitrogen (N_2) are major detonation products of high explosives and it has long been conjectured that they may phase segregate at high enough temperatures and pressures to influence detonation properties of common explosives. We analyze the phase diagram of H_2O-N_2 mixtures using a thermodynamic theory for polar-nonpolar mixtures and find that phase segregation is unlikely to occur above approximately 1600K. Therefore, H_2O-N_2 immiscibility is not likely to be relevant for detonation predictions. We propose instead that the high pressure ionic dissociation of water plays an important role in detonation, and model it using a new ionic thermodynamics. We employ this model in chemical equilibrium calculations of standard high explosives, e.g. PETN, HMX and RDX, and find that it performs very well under a wide range of conditions. Thus, although it may require further development, it is likely that explicitly ionic thermodynamics will become a standard tool for explosives modeling.

Introduction

Predicting the detonation properties of high explosives and explosive formulations remains a subject of much practical and fundamental scientific interest despite its considerable history [1, 2]. A major part of this problem is the calculation of the equation of state of detonation products, which largely determines the Chapman-Jouguet (CJ) state and expansion characteristics of any explosive. Following early empirical developments such as the JWL equation of state [2], more accurate models of the thermodynamics of detonation products have been enabled by advances in the statistical mechanics of fluid mixtures. Equations of state that rely on realistic representations of the inter-particle interactions [3-6] are now accepted as the gold standard for explosives modeling due to their proven predictive power. The advent of quantum simulation methods has recently provided however new insights into the behavior of molecular fluids at pressures and temperatures characteristic of detonation, which also need to be incorporated into any predictive model.

In the present work we discuss, based on recent theoretical and computational results, our current view on two fundamental effects in the thermodynamics of detonation products. One is the supercritical phase separation of nitrogen and water, which has been studied up to temperatures of about 800K [7]; this transition has also been previously conjectured to occur at CJ conditions [6], thus potentially playing an essential role in detonation modeling. The other effect that we focus on is the ionic dissociation of water, which has been found to occur in quantum molecular dynamics (QMD) simulations, both under shock

conditions and in detonation products mixtures [8-9]. This behavior has also been long discussed as the only plausible explanation for the electrical conductivity of water under shock conditions [10], and it may also occur in other hydrogen bonding fluids such as HCl, HF, etc.

Phase segregation versus ionic dissociation

The detonation of modern condensed high explosives yields complex multiphase, multicomponent mixtures which are generally understood to reach chemical equilibrium very rapidly behind the shock front. Although some carbon rich explosives, most notably TNT and TATB, also produce significant amounts of condensed carbon, the major detonation products are usually small molecules mixed in a supercritical fluid phase. This dense, hot fluid typically consists of significant amounts of N_2, H_2O, CO_2, CO, NH_3, H_2, etc. The thermodynamical properties of this mixture play a crucial role in determining the detonation velocity of explosives as well as the work that they can deliver upon subsequent expansion, and therefore their prediction is a major task of explosives modeling [1-6].

The equation of state of such mixtures can be best calculated in a wide range of pressures, temperatures and compositions using statistical mechanics fluid theories that employ realistic, well tested intermolecular potentials. The exp-6 potential has proven to be particularly useful for this task since it captures correctly the inter-molecular repulsions that are dominant at high densities:

$$V(r) = \frac{\varepsilon}{\alpha - 6} \left\{ 6 \exp\left[\alpha(1 - r/r_0)\right] - \alpha\left(r_0/r\right)^6 \right\}$$

When employed in a suitable mixture theory, under the assumption of chemical equilibrium, it usually allows correct predictions for a wide variety of systems, from detonating explosives to reactive shock Hugoniots. Such calculations were performed for example by Ree [6], who showed that they can reproduce the experimental data available for some common high explosives, including PETN. He also found however that

analogous calculations were less successful for HMX-based formulations like PBX9404, although the composition of the detonation products at the CJ point was to a large extent similar. The theoretical predictions also seriously overestimated the experimental shock Hugoniot of PBX9404, which is significantly more compressible than predicted. Given that the detonation temperature of PBX 9404 is lower than that of PETN while its detonation pressure is higher, Ree conjectured that the discrepancy was due to the occurrence of a supercritical phase separation of nitrogen and water at temperatures as high as 4000K. This was later introduced in the calculations via an empirical correction of the nitrogen-water interaction, and agreement with experiments was to a reasonable extent restored. The interaction correction was based on the premise that the phase separation was due to significant positive non-additivity of the pair interactions, i.e.

$$r_{N_2-H_2O}^0 > \frac{r_{N_2}^0 + r_{H_2O}^0}{2}$$

Thus it was assumed that N_2-H_2O phase segregation is largely an entropic effect, similar with the one encountered in non-additive hard sphere mixtures.

Supercritical phase separations are a common occurrence for a wide range of fluid mixtures, and such a phase transition is well documented for nitrogen-water systems at temperatures as high as about 800K and pressures up to approximately 2GPa [11]. Unfortunately they remain quite difficult to predict theoretically, largely because such phase transition lines result from an equality of chemical potentials and are therefore quite sensitive to any uncertainties in the interactions. The unlike-pair potentials can play an important role in determining phase separation, but they are difficult to determine with any degree of certainty. Theoretical efforts are further hampered by a lack of equation of state experimental data on mixtures at high pressures, which could be used to provide direct constraints on these interactions.

The like-pair potentials however also play crucial roles in determining phase boundaries, and need to be well understood and modeled if reasonable estimates are to be made. The exp-6

potential has long been proven to enable accurate calculations of the high pressure-high temperature thermodynamics of simple molecules, and remains the best representation of inter-molecular interactions at these conditions. Polar molecules on the other hand have been always challenging to model within the constraints of a simple exp-6 potential. Indeed, for his water modeling Ree [6] adopted an empirical adjustment in which the strength of the interaction was assumed to be temperature dependent. Unfortunately such approximations further limit the reliability of phase boundary calculations.
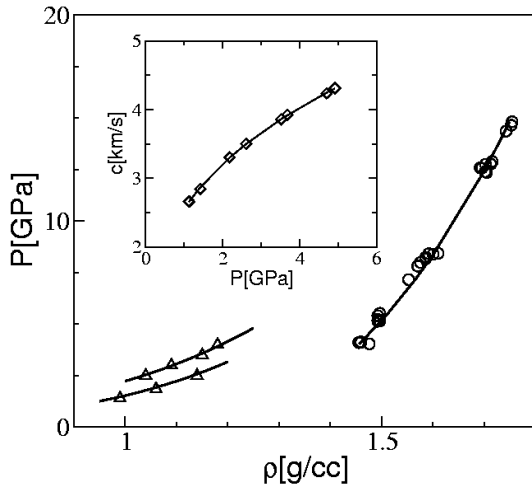

Fig.1 Experimental data (symbols) and exp6-polar thermodynamics results (lines) for dense, supercritical water. Triangles: T=983K and T=1373K isotherms; circles: shock Hugoniot; inset: sound speed at T=673K.

We have recently developed a new, more physical approach for the thermodynamics of polar molecules in which the electrostatic interactions are treated as perturbations of the exp-6 potential [5]. In terms of the Helmholtz free energy per particle f, this approach can be summarized as follows:

$$f = f_{\exp-6} + \Delta f_{dipoles}$$

Here f_{exp-6} is the free energy of the reference system, and $\Delta f_{dipoles}$ is a perturbative correction due to the dipole-dipole interactions. When applied to

water this treatment enables accurate calculations for a wide range of equation of state data – see Fig. 1, as well as diffusion, dielectric constants, and to some extent even fluid structure. Moreover, it can be easily generalized to polar-nonpolar mixtures such as nitrogen-water. We employed the new theory to examine phase segregation in this system. The nitrogen-water interaction was assumed to follow from standard combination rules, i.e. without arbitrary additivity corrections such as that introduced in [6] to induce the occurrence of phase segregation at detonation conditions.

We find that phase coexistence is indeed predicted by the exp6-polar thermodynamic theory. The results of the calculations – solubility curves for the N_2-H_2O system as a function of temperature - are summarized in Fig. 2. Although both these calculations and those of Ref. 6 indicate the existence of phase separation, both the origin and the predicted features of this transformation are different. As opposed to Ref. [6], here the phase transition is largely an energy not entropy driven occurrence, due to the energy-lowering effect of dipole-dipole interactions. In fact, slightly better agreement with the low temperature experimental results could be obtained with a very small *negative, not positive* N_2-H_2O non-additivity.
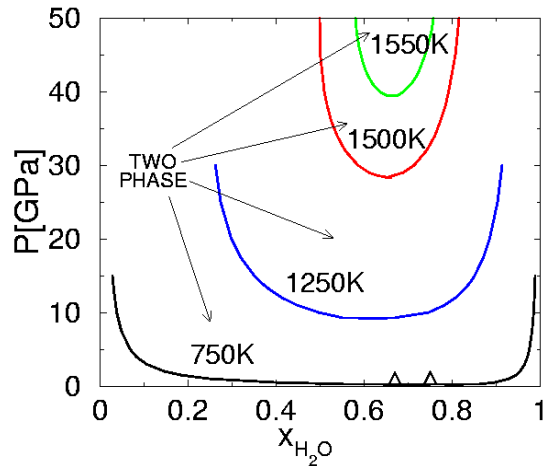

Fig. 2 Phase coexistence diagram for N_2-H_2O mixtures at temperatures between 750K and 1550K calculated using the exp6-polar mixture theory (solid lines); triangles denote the experimental data of Ref. 7.

Even more importantly, the phase diagram differs in some major respects from that of Ref. [6]. There the nitrogen-water coexistence region remains essentially identical up to temperatures as high as 4000K, and it only moves to higher pressures as the temperature is increased. On the other hand, as shown in Fig. 2, the present calculations predict that the miscibility gap narrows strongly at higher temperatures, with the net result that above approximately 1600K the two fluids become fully miscible at all pressures. This behavior is in agreement with the theoretical calculations reported in [12] and, moreover, the results also agree better with the available experimental data [7].

Nevertheless, due to inherent uncertainties in modeling, mainly due to the usage of simple effective classical potentials in a wide range of pressures and temperatures, we cannot establish conclusively that phase segregation of nitrogen and water at high pressures and temperatures does indeed have the features suggested by the present results. However, we should note that this thermodynamic modeling is the most physical to date, and it does not employ any arbitrary assumptions. Furthermore, the simulations of Ref. [13] also suggest that, just as in the above calculations, the dipole moment of water and not the unlike-pair non-additivity is in fact the major driving force for phase separation. Experimental results at higher pressures and temperatures would be very useful in fully elucidating this issue, particularly because the relevant thermodynamic regime is now within the reach of new high pressure-high temperature techniques.

We consider next the consequences of these calculations for the modeling of high explosives. To this end we determine the CJ points and expansion isentropes of three common explosives: PETN ($C_5H_8N_4O_{12}$), HMX ($C_4H_8N_8O_8$) and RDX ($C_3H_6N_6O_6$). The results are shown in Fig. 3 together with the phase coexistence boundary for a typical nitrogen-water relative concentration encountered in detonation products. They indicate that both the CJ points and the major parts of the isentropic expansion paths are well outside the nitrogen-water immiscibility region. Phase separation appears therefore to be potentially relevant only for strongly expanded

states, or practical situations where strong confinement is maintained to very low temperatures.
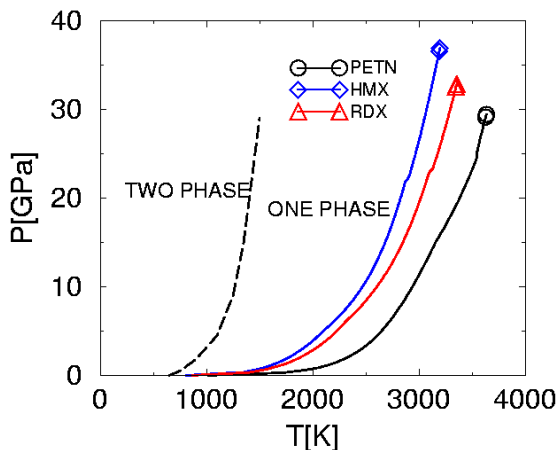

Fig. 3 Chapman-Jouguet expansion isentropes of PETN, RDX and HMX and the coexistence boundary of the $33\%N_2+67\%H_2O$ water mixture.

Phase separation as a possible high pressure-high temperature effect was originally proposed due to the difficulty in modeling detonation product mixtures with large water and nitrogen content. Although the previous analysis strongly suggests that this effect is not operational at detonation conditions, difficulties remain in accurately predicting the behavior of water-rich mixtures at high pressures and temperatures.

Quantum molecular dynamics (QMD) simulations of hydrogen bonding liquids, e.g. H_2O, HCl, HF, etc., [8] indicate that at extreme conditions these systems exhibit a behavior that is different from what is traditionally assumed for molecular fluids. For such systems the breaking of molecular bonds that occurs upon the application of high pressures and temperatures, e.g. 10's of GPa and 1000's of K, leads to the formation of small products, in particular hydrogen (H), that carry an effective electrical charge. As a result, the process can be understood as ionic dissociation, although the resulting ionic products are better treated as radicals rather than ions in solution [9]. This has important consequences for the equation of state of these fluids, as well as their conduction properties [8-9]. Direct QMD simulations of PETN [9] at CJ conditions indicate in fact that

water ionic dissociation is also likely to appear at detonation conditions, in agreement with experimental results on the electrical conductivity of detonation products [14].

We have previously proposed and tested for model ionic mixtures an explicitly ionic thermodynamics that treats the charge-charge interactions at the perturbation level [4]. This thermodynamic concept is now largely integrated in chemical equilibrium calculations and we test it here first on water.

To this end we calculate the shock Hugoniot of water, which has been measured with good accuracy experimentally [15], and for which detailed QMD simulations are also available [8]. Our theoretical chemical equilibrium calculations include H_2O modeled using the exp6-polar thermodynamics, as well as OH^- and H^+ radicals [16]; their parameters are listed in Table 1.

Table 1. Water interaction parameters

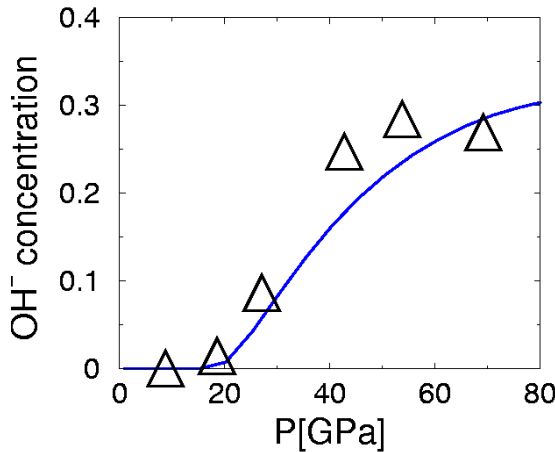|	$\varepsilon[K]$	$r_0[A]$	α	$\mu[D]$	$q[e]$
H_2O	222	3.54	11.5	2.19	0
OH^-	320	3.20	13.6	0	−0.365
H^+	320	0.65	13.6	0	+0.365

The calculation results are shown in Figs. 4 and 5.

Fig. 4 Molar fraction of OH^- ions along the shock Hugoniot of water: QMD simulations of Ref. 8 (triangles) and exp6-polar ionic thermodynamics (solid blue line).

We find that the H_2O concentration decreases, while the concentration of ions steadily increases at high pressures. This behavior is in qualitative and reasonably good quantitative agreement with the QMD simulations – see Fig. 4. Moreover, the introduction of ions leads to improved modeling of the shock Hugoniot – see Fig. 5, compared with calculations assuming no such break-up. The subtle "softening" of the Hugoniot curve around 15-20 GPa thus appears to be due to the inception of ionic dissociation, as observed in QMD simulations [8] and also suggested by conductivity measurements [10].
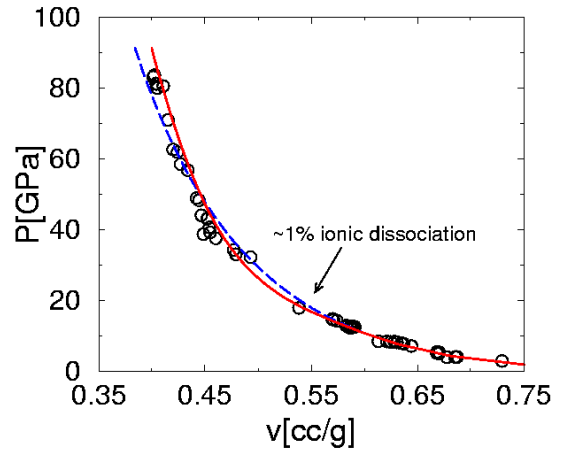

Fig. 5 Water shock Hugoniot: experimental data (circles), exp6-polar thermodynamics without ions (dashed blue line) and exp6-polar ionic thermodynamics (solid red line).

High explosive modeling via explicitly ionic thermodynamics

We now test the predictions of the ionic thermodynamics model for water dissociation in the context of detonation calculations for a set of standard CHNO high explosives. Indeed, it is likely that for such systems the most important ionic products are OH^- and H^+ radicals, since H_2O is the only major molecular product likely to undergo ionic dissociation at high pressures. The ionic modeling of compounds containing large amounts of chlorine and/or fluorine on the other hand will probably require that Cl^- and F^- radicals also be considered.

The present calculations were performed using the thermochemical code Cheetah [3]. We focused on PETN, HMX and RDX, as well as an HMX-based composition, PBX9404 (HMX 94% + nitrocellulose 3% + CEF 3%), for which shock Hugoniot data are available to high pressures. The detonation velocity results for these compounds are shown in Table 2; they indicate very good agreement with experiments.

Table 2. Detonation velocity of high explosives

HE	ρ_0[g/cc]	D_{exp}[km/s]	D_{theor}[km/s]
PETN	1.763	8.28	8.34
HMX	1.894	9.12	9.26
RDX	1.846	8.80	8.88
PBX9404	1.767	8.64	8.68

The predicted CJ composition for PETN is also shown in Fig. 6. We find that a majority of water molecules are likely to dissociate, and that the concentration of ions is therefore significant at detonation conditions.
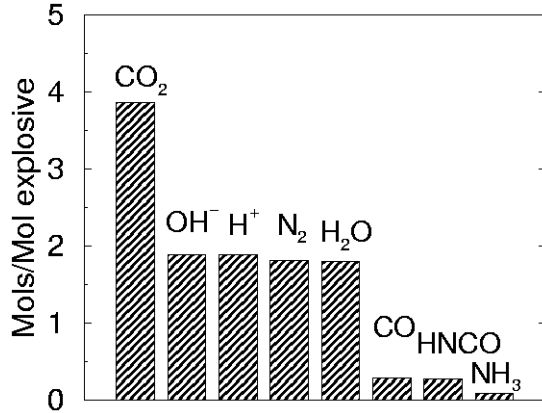

Fig. 6 Calculated composition of the detonation products at the Chapman-Jouguet point of PETN.

To further test this prediction we also calculate the ionic conductivity of PETN at the CJ point, by employing the Nernst-Einstein relation, which connects the individual concentrations and diffusion constants to the conductivity:

$$\sigma = \left(n_{H^+} q_{H^+}^2 D_{H^+} + n_{OH^-} q_{OH^-}^2 D_{OH^-} \right) / k_B T$$

The diffusion constants of the OH^- and H^+ ions were estimated using entropy scaling concepts [17]. The calculated conductivity is 70 $\Omega^{-1}m^{-1}$, which is in good agreement with the measured value of 60 $\Omega^{-1}m^{-1}$ [14]. This further indicates that the predicted contribution of ions to chemical equilibrium is likely to be at least qualitatively correct.
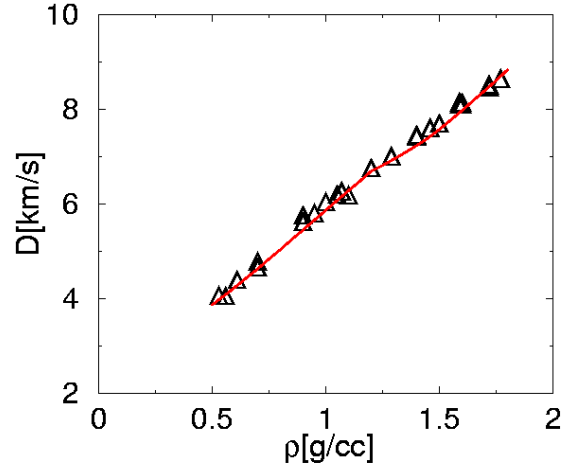

Fig. 7 Detonation velocity of RDX as function of initial density: triangles (experimental data quoted in Ref. 6) and exp6-polar ionic thermodynamics (solid red line).
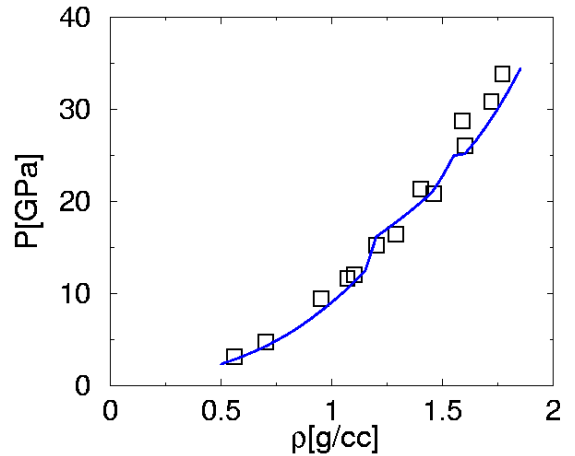

Fig. 8 Chapman-Jouguet pressure of RDX as function of the initial density: squares (experimental data quoted in Ref. 6) and exp6-polar ionic thermodynamics (solid blue line).

We consider next the detonation behavior of RDX as a function of the initial density. The experimental data available for its detonation velocity and pressure cover a very wide range of initial densities, from 0.53 g/cc to 1.77 g/cc. Since the CJ pressure varies an order of magnitude from the lowest to the highest initial density, this is a very stringent test of the ionic thermodynamics. The results shown in Fig. 7 indicate excellent agreement for the detonation velocity over the entire range. Moreover, the calculated CJ pressures also agree very well with the measured ones – see Fig. 8.

We also analyze an explosive formulation based on HMX, PBX9404, which due to its higher detonation pressures and lower temperatures than PETN was originally believed to be difficult to model accurately without N_2-H_2O phase separation. We show in Fig. 9 the experimental shock Hugoniot of PBX9404, along with the one calculated using the ionic thermodynamics. The results are good, without any of the very large discrepancies previously reported for single fluid phase calculations.
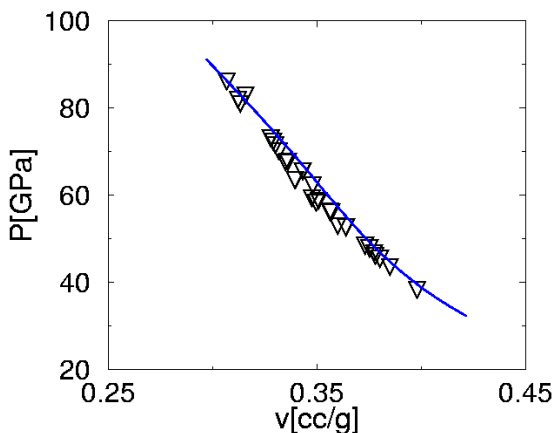

Fig. 9 Shock Hugoniot of PBX9404: experimental data (black diamonds) and ionic thermodynamics (blue triangles).

Conclusions

It has been long conjectured that nitrogen-water phase separation plays an important role in determining the detonation properties of CHNO explosives. Using a statistical mechanics theory for polar-nonpolar mixtures we calculate the phase diagram of N_2+H_2O mixtures and find that nitrogen and water are likely to become fully miscible above approximately 1600K. Thus, phase separation is unlikely to be relevant for detonation predictions, although it may still be important for some expanded states away from the principal adiabat. We propose instead that the ionic dissociation of certain molecular products, in particular water, needs to be accounted for in detonation calculations. Using an explicitly ionic thermodynamics we find that we can accurately model the behavior of water at high pressures, including its ionic break-up along the shock Hugoniot. When integrated into chemical equilibrium calculations this approach leads to very good predictions for common high explosives under a wide range of thermodynamic conditions. It is therefore likely to become a standard tool in detonation modeling.

Acknowledgements

References

1. Ia.B. Zeldovich and A.S. Kompaneets,, "*Theory of Detonation*", Academic Press, New York and London (1960).
2. W. Fickett, W.C. Davis, "*Detonation*", University of California Press, Berkeley (1979).
3. L.E. Fried, W.M. Howard, P.C. Souers, "*EXP6: A new equation of state library for high pressure thermochemistry*", Proc. 12th Int. Det. Symp. (2002).
4. S. Bastea, K.R. Glaesemann, L.E. Fried, "*Equation of state for high explosives detonation products with explicit polar and ionic species*", Proc. 13th Int. Det. Symp. (2006).
5. S. Bastea, L.E. Fried, "*Exp6-polar thermodynamics of dense supercritical water*", J. Chem. Phys. **128**, 174502 (2008).

6. F.H. Ree, "*Supercritical fluid phase separations: Implications for detonation properties of condensed explosives*", J. Chem. Phys. **84**, 5845 (1986).

7. S. Costantino, S.R. Rice, "*Supercritical phase separation in water-nitrogen mixtures*", J. Phys. Chem. **95**, 9034 (1991).

8. N. Goldman, E.J. Reed, I-F.W. Kuo, L.E. Fried, C.J. Mundy, A. Curioni, "*Ab initio simulation of the equation of state and kinetics of shocked water*", J. Chem. Phys. **130**, 124517 (2009) and references therein.

9. C.J. Wu, L.E. Fried, L.N. Yang, N. Goldman, S. Bastea, *"Catalytic behavior of dense hot water"*, Nature Chemistry **1**, 57 (2009).

10. R. Chau, A.C. Mitchell, R.W. Minich, W.J. Nellis, "*Electrical conductivity of water compressed dynamically to pressures of 70-180 GPa (0.7-1.8 Mbar)*", J. Chem. Phys. **114**, 1361 (2001).

11. J.A. Schouten, "*What is different in mixtures? From critical point to high pressures*", Int. J. Thermophys. **22**, 23 (2000) and references therein.

12. S.V. Churakov, M. Gottschalk, "*Perturbation theory based equation of state for polar molecular fluids: II. Fluid mixtures*", Geochim. Cosmochim. Ac. **67**, 2415 (2003).

13. A. Maiti, R. H. Gee, S. Bastea, L.E. Fried, "*Phase separation in N_2-H_2O mixture: Molecular dynamics simulations using atomistic force fields*", J. Chem. Phys. **126**, 044510 (2007).

14. B. Hayes, "*On electrical conductivity in detonation products*", Proc. 4th Int. Det. Symp. (1965).

15. S.P. Marsh, "*LASL Shock Hugoniot Data*", University of California Press, Berkeley (1980).

16. The charges carried by OH^{-} and H^{+} are set to the values observed in QMD simulations [8], resulting from electronic charge equilibration. Although further theoretical development may be necessary, this approach is suggested by the small variation of the effective charge of H^{+} with pressure [8], or reactive environment [9] (for typical high explosives). In addition, JANAF values were used for all heats of formation and standard entropies, except for H^{+}, where a reduced value of 55 kJ/mol was used to account for charge delocalization at high densities.

17. S. Bastea, "*Transport properties of dense fluid argon*", Phys. Rev. E. **68**, 031204 (2003).